I. SYNTHESIS AND REACTIONS OF o-QUINONE DIIMIDES

II. STUDIES ON THE STRUCTURE OF QUASSIN

BY

CHARLES NATHAN WINNICK

B.S., Massachusetts Institute of Technology, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. SYNTHESIS AND REACTIONS OF o-QUINONE DIIMIDES

Introduction

The successful synthesis of *p*-quinonedibenzensulfonimide has stimulated interest in the field of quinonediimides (1). Although *p*-quinonediimine has been synthesized and *o*-quinonediimine obtained in solution, the great instability of these compounds renders them unsuitable for synthetic work. Since the *p*-quinonedibenzenesulfonimides are readily obtained by oxidation of the corresponding *p*-phenylenedibenzenesulfonamides with lead tetraacetate, it was of interest to apply this reaction to the ortho series. Another objective of this investigation was the study of the addition of hydrogen cholride to *o*-quinonedibenzenesulfonimides, in order to determine which of the possible isomers is formed.

Discussion Of Results

The oxidation of 4-chloro-, 4-methyl-, 3-methyl-, and 4,5-dichloro-*o*-phenylenedibenzenesulfonamides with lead tetraacetate in acetic acid led to the corresponding *o*-quinonedibenzenesulfonimides. The oxidation of 3,5-dimethyl- and 4,5-dimethyl-*o*-phenylenedibenzenesulfonamides to the diimides with lead tetraacetate was found to proceed better in acetic anhydride. 3,4,5-Trichloro-*o*-phenylenedibenzenesulfonamide was oxidized to the diimide with lead tetraacetate in anhydrous ether.

The 4-chloro-, 4-methyl-, 3,5-dimethyl-, and 4,5-dimethyl-*o*-quinonedibenzenesulfonimides were reduced to the corresponding diamides with zinc and acetic acid. 4-Methyl-*o*-quinonedibenzenesulfonimide was also reduced to the diamide with sulfur dioxide in water. The addition of hydrogen chloride to the 4-methyl- and 4-chloro-*o*-quinonedibenzenesulfonimides in acetic acid takes place very readily. A mixture of isomers is formed in each case which could not be separated

by fractional crystallization. These mixtures were purified by conversion to the potassium salts, recrystallization of the salt and acidification. The major components of these mixtures were shown to be 4-methyl-5-chloro- and 4,5-dichloro-*o*-phenylenedibenzenesulfonamide, respectively. These compounds were synthesized by unequivocal methods. The addition of hydrogen chloride to 3,5-dimethyl-*o*-quinonedibenzenesulfonimide gave only one of the possible isomers and this was proven to be 3,5-dimethyl-4-chloro-*o*-phenylenedibenzenesulfonamide by independent synthesis. Addition of hydrogen chloride to the 4,5-dimethyl-, 4,5-dichloro-, and 3,4,5-trichloro-*o*-quinonedibenzenesulfonimides was also carried out, but in these cases isomer formation is not possible. It was found that the addition of hydrogen chloride to the 4-methyl- and 4-chloro-*o*-quinonedibenzenesulfonimides in dioxane produces a different mixture of isomers from that obtained in acetic acid. The mixtures from dioxane are always lower melting than those from acetic acid. The purification of the mixtures from dioxane was not attained.

Attempts to oxidize *o*-phenylenedibenzenesulfonamide did not give the desired diimide but complex, unidentified oxidation products. 4-Nitro-*o*-phenylenedibenzenesulfonamide was found to be stable to the action of lead tetraacetate.

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II. STUDIES ON THE STRUCTURE OF QUASSIN

Introduction

Quassin, a bitter principle extracted from the wood of the quassia tree, has been known for over a hundred years. Previous investigations have not elucidated its structure.

Recent work in This Laboratory (1) has shown quassin to be a mixture of two substances, isoquassin and neoquassin, which are in the relationship of a ketone to a tertiary alcohol. The presence of unsaturation, a lactone grouping, methyl groups and methoxyl groups has been demonstrated. Recently, other investigators have postulated that only the oxidized form, isoquassin, is a lactone (2). They believe that neoquassin is a hemiacetal formed by reduction of the lactone carbonyl of isoquassin.

Discussion Of Results

Crude quassin was purified according to the method of Whaley. Oxidations of quassin with nitric acid and with chromic anhydride were carried out. Oxidation with nitric acid gives oxalic acid which was removed as the silver salt, and an amorphous product which could not be satisfactorily purified or identified. Oxidation with chromic anhydride in acetic acid led to the isolation of two fractions. An acidic fraction isolated as the silver salt was converted into a *p*-bromophenacyl ester which was easily purified, but whose analysis could not be interpreted. A ketonic fraction, evidently a mixture, was isolated as the 2,4-dinitrophenylhydrazones which were difficult to purify. Chromatography of these 2,4-dinitrophenylhydrazones gave a major fraction which, from its nitrogen analysis, corresponds to a ketone of molecular weight 223. Zinc dust distillation of quassin yielded a crystalline product whose infrared spectrum was different from that of quassin but which was not further characterized.

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VITA

The author was born on December 15, 1925 in Hartford, Connecticut. He attended the public schools of that city graduating from Weaver High School in 1943. He entered the Massachusetts Institute of Technology in 1943 and left in 1944 to enter the armed forces. He re-entered the Massachusetts Institute of Technology in 1946 receiving the degree of Bachelor of Science in 1948. He entered the Graduate School of the University of Illinois in 1948 and received the degree of Master of Science in 1949.

The author was a teaching assistant during 1948-1949. He held the Standard Oil Company (Indiana) fellowship during 1949-1950 and the Eastman Kodak Company fellowship during 1950-1951.

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